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Replacing Critical and Strategic Refractory Metal Elements in Nickel-Base Superalloys

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Joseph R. Stephens, Robert L. Dreshfield, and Michael W. Nathal
Lewis Research Center
Cleveland, Ohio

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Replacing Critical and Strategic Refractory Metal Elements in Nickel-Base Superalloys

Joseph R. Stephens, Robert L. Dreshfield, and Michael V. Nathal
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

ABSTRACT

The United States imports over 90 percent of the cobalt, chromium, tantalum, and niobium that is required for domestic consumption. Nickel-base superalloys that contain these metals as alloying elements are essential in high performance gas turbine engines required for today's civilian and military aircraft. These four alloying elements have been identified as strategic and critical in the aerospace industry. NASA has undertaken a fundamental program called COSAM - Conservation of Strategic Aerospace Materials aimed at reducing the need for strategic materials in gas turbine engines. Technological thrusts in two major areas are under way and include strategic element substitution and alternative material identification. This paper will provide a summary of the adoption of refractory metals in nickel-base superalloys including their roles in mechanical strengthening and environmental resistance; present the current research activities under way in the COSAM Program; and summarize the research findings to date.

THE PURPOSES OF THIS PAPER are to review the use of refractory metals in nickel-base superalloys and to describe NASA's research activities in replacing those refractory metals that are considered to be critical and strategic to the aerospace industry.

As a working definition of critical and strategic metals, we use the following: those predominantly or wholly imported elements contained in the metallic alloys used in aerospace components which are essential to the strategic economic health of the U.S. aerospace industry. As a result of meetings with the ASME Gas Turbine Panel in 1979 and a survey of aerospace companies in 1980, we have focused primarily on the aircraft engine industry's needs. Based on these and further discussions with several aircraft engine manufacturers, four elements emerged that were of particular concern. The alloys used to

build the critical high temperature components for aircraft propulsion systems require the use of the three refractory metals Cr, Ta, and Nb plus Co. These metals are contained in superalloys, steels, and stainless steels that are used in engine manufacturing. The location of these metals in aircraft engine compressors, turbines, and combustors is illustrated in Fig. 1. Typical requirements by weight are shown in Fig. 2 for the F-100 engines. The need for such materials has increased as the demands have grown for higher durability, higher performance, fuel efficient aircraft turbine engines. Because of the essential nature of these metals and in order for the U.S. aircraft industry to maintain its competitive position, it is necessary that supplies be readily available at a reasonably stable cost. To achieve these requirements, domestic sources of key metals are desirable. However, the United States has never been self-sufficient in these metals. Today, we are almost totally dependent on foreign sources for these metals (ref. 1). Therefore, the U.S. aircraft engine industry can be seen to be highly vulnerable to supply instabilities of the essential metals for engine manufacturing. Accompanying supply disruptions or increased demand are price changes of several hundred percent as shown in Fig. 3 (after ref. 2). These rapid price increases illustrate the vulnerability of the U.S. aircraft engine industry to cost fluctuations. The essential nature of Cr, Ta, Nb, and Co, along with their vulnerability to supply instabilities and cost fluctuations, combine to cause these metals to be classified as critical and strategic aerospace metals. Their sensitivity to total disruption during a time of worldwide crisis is, of course, readily recognizable.

This reliance on the importance of the strategic metals used in today's military and commercial aircraft engines poses a threat to the national security of the United States. This view has been expressed by many sectors of the materials industry. For example, E. F. Andrews, Vice President of Allegheny International said, "The national security and economic survival of the

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United States depend upon the nation's capability to secure an uninterrupted flow of critical minerals from politically unstable third world nations" (ref. 3). Former Secretary of Interior James Watt was quoted as saying, "I considered energy to be the extreme problem of the '70's; minerals are going to be the problem of the '80's" (ref. 3).

The metals discussed herein also are vital to the welfare of the nation's economy since aerospace sales are a major positive contributor to our balance of payments (ref. 4). Thus, the continued availability of critical elements at a reasonable cost is a national issue which requires cooperative action between industry and appropriate government agencies. In order to offset or minimize possible future disruptions in supply, efforts to develop viable options must be pursued aggressively since a new material can take from 6 to 9 years of research and development efforts before qualifying for such aerospace service. Thus, a long term commitment to the creation of a sound technology base upon which to respond to interruptions or price fluctuations is in the best national interest.

NASA Lewis Research Center has undertaken a long-range program in support of the aerospace industry aimed at reducing the need of critical and strategic materials used in gas turbine engines (refs. 5 to 8). The program is called COSAM - Conservation of Strategic Aerospace Materials. This program has three general objectives. These are to (1) contribute basic scientific understanding to the turbine engine "technology bank" so as to maintain our national security in possible times of constriction or interruption of our strategic material supply lines; (2) help reduce the dependence of United States military and civilian gas turbine engines on disruptive worldwide supply/price fluctuations in regard to strategic materials; and by these research contributions (3) help minimize the acquisition costs as well as optimize the performance of such engines so as to contribute to the United States position of preeminence in world gas turbine engine markets.

We will present a brief history of the introduction of refractory metals in nickel-base superalloys, describe the specific research activities under way with the COSAM Program aimed at reducing the use of the critical and strategic refractory metals, and discuss research results available to date.

HISTORY OF REFRACTORY METAL ALLOYING

INTRODUCTION INTO SUPERALLOYS - Later in this conference we will hear three sessions solely devoted to the physical and mechanical metallurgy of the refractory metals in superalloys. At this point we feel it would be of interest to briefly review chronologically the history of refractory metal additions to the nickel-base superalloys. We will restrict our definition of refractory metals to Groups V, VI, and VII elements (fig. 4) and accept that the Ni-base superalloys were "born" with 20 wt% Cr

(ref. 9) in an 80 wt% Ni alloy for electrical heating elements at around the beginning of this century.

In 1926, Heraeus Vacuumschmelze A. G. received a patent for a nickel-chromium alloy which may contain up to 15 wt% W and 12 wt% Mo. The purpose of the refractory metal additions was to raise the yield point (ref. 9). As late as 1930, however, Campbell (ref. 10) failed to show either W or Mo as major alloying elements either for resistance alloys or for heat-resisting alloys. Inspection of his "resistance alloy" list reveals one resistance alloy containing 1 to 2 wt% W. His nickel-base "heat resisting alloys" list has one "nichrome" containing 1.33 wt% Mo and an alloy designated "Pyros" containing 5 wt% W. There are also two Fe-base "heat-resisting alloys" containing either W or Mo additions. Campbell's list also shows that by 1930, the use of Mo and W was widely accepted in Co-base alloys.

The principal impetus for superalloy development has been the aircraft gas turbine engine (refs. 9 and 11). The first age-hardenable Ni-base superalloy to be commercially produced was Nimonic 80*, an age-hardening Ni - 20 wt% Cr alloy. In 1940 a British patent was filed by Pfeil (ref. 9) for a heat treatable alloy of at least 20 wt% Mo and/or W. In the late 1940's Gresham et al., in Great Britain showed that Mo additions benefitted Ni-base superalloys, but commercial exploitation of Mo additions waited until 1955 - the introduction of Nimonic 100 (ref. 11). In the early 50's, the alloys being introduced in the United States, such as Waspaloy**, were alloys containing about 5 wt% Mo (ref. 11). The only commercially significant alloy to use V is IN-100, which became available in about 1960. In the early 60's, W and Ta were widely accepted for alloying in Ni-base alloys. On the other hand, Inconel 713C (a casting alloy) containing 2 wt% Nb was available before the end of the 50's. Demonstration of the effectiveness of Re addition to Ni-base alloys occurred in the late 60's (ref. 12).

The increasing use trend for refractory metals is shown in Fig. 5 and table I. It is apparent that, on a weight basis, the refractory metal content of Ni-base superalloys tended to steadily increase from the mid-40's to about 1980. The maximum content was in alloy TRW-NASA VIA, which was developed in the mid-60's. If the trend is viewed on an atom basis, Fig. 5(b) shows the use of refractory metals increased from 1 to about 6 at.% in less than one decade. Except for René 150, which contains nearly 8 at.% refractory metals, it appears that TRW-NASA VIA represents a maximum of 6.6 at.% and more recent alloys have, in fact, used slightly lower amounts of refractory metals. A reason for the slight decrease from 6.6 at.% will be offered in brief discussions of the physical metallurgy of re-

*Nimonic is a tradename of the International Nickel Company.

**Waspaloy is a tradename of United Technologies Corporation.

fractory metal additions to nickel-base superalloys which follows.

REFRACTORY METALS AND PROPERTIES - In the early years of superalloy development, the goal was clearly to advance operating temperatures. This of course also increased the strength level at constant temperatures. The early use of virtually all the refractory metals was in fact intended to improve creep-rupture and other high temperature mechanical properties. Because the alloy improvements were made by combinations of increasing γ' content, the principal strengthener in Ni-base superalloys, and refractory metal content, the improvements due to each are confounded.

The work of Freche (ref. 13) and his co-workers in the early 60's did demonstrate that additions of V and Ta were beneficial to the tensile strength and stress-rupture life of Ni-base superalloys at 980° C. During the development of alloy TRW-NASA VIA (ref. 14), it was shown that W and Ta could improve stress-rupture life at 1095° C. Subsequently, the benefit to stress-rupture life of small Re additions was established by Collins (ref. 15) for the same alloy. More recently, Lin (ref. 16) has shown that Re additions could also improve creep-rupture life of an alloy similar to MAR-M 200.[†]

As the operating temperature of gas turbines increased, the Cr level of the advanced alloys decreased. This can be seen in table I by comparing the 20 wt% Cr of Nimonic 80A to the 5 to 10 wt% Cr of alloys such as René 150 or P&WA 454. The result of these combinations was that the turbine blade life became limited more by surface stability than mechanical failure. The first alloy to encounter the problem was Nimonic 100 (ref. 9), which was quickly replaced by Nimonic 105 having about 5 wt% more Cr. In the new alloys Ta and Nb are reported to be beneficial to surface stability (refs. 17 and 18); however, Cr and Al are the primary elements to control oxidation and corrosion resistance of the alloys.

It should therefore be recognized that, while the prime motive in refractory metal addition to Ni-base superalloys has been to increase strength levels, both Ta and Nb additions can also be beneficial to the alloy's surface stability.

PHYSICAL METALLURGY OF REFRACTORY METAL ADDITIONS - The modern Ni-base superalloys are composed of a face-centered-cubic (FCC) Ni-rich solid solution called γ ; 20 to 65 vol% of Ni_3Al , Ti - an ordered-FCC phase called γ' ; and a small amount of a variety of carbides; in the higher B-containing alloys, some borides may also be present. After prolonged exposure to elevated temperature σ , μ , Laves, and body-centered-cubic (BCC) phases such as α -W may also be observed. The amount, size, and distribution of the γ' together with its lattice mismatch relative to the γ phase are generally accepted as being the principal parameters governing the mechanical behavior of the alloys. In addition, the amount and morphology of the minor phases can have a

profound influence on some mechanical properties. For detailed reviews of the physical and mechanical metallurgy of Ni-base superalloys, readers are referred to Refs. 9, 11, and 19 to 21.

During the period 1940 to date, the use temperature has increased at a rate of about 9° C per year as shown in Fig. 6. This has been accomplished through the combined effects of improved chemistry and innovative processing. While the principal chemical changes increased the amount of γ' to greater than 50 vol% (by Al and Ti additions) in the most advanced blade and disk alloys, the importance of the refractory metals cannot be overlooked. Mo, W, and Nb are regarded as effective solid solution strengtheners which act to principally strengthen the γ phase (refs. 9 and 13). The maximum solubility of the refractory elements in Ni (ref. 19) is shown in table II. It can be seen that these metals have high solubility in the γ , although in γ' -saturated γ the levels are significantly reduced. For example, in a series of experimental superalloys, only 8.7 at.% Mo and 5 at.% W were found to be soluble in γ at 850° C (ref. 22). These levels are significantly below the maximum solubility shown in table II (refs. 23 and 24). Either Mo- or W-rich solid solution phases were observed to precipitate in some of the experimental superalloys. It was suggested that if the alloy contained less than 67 at.% Ni (+ Co) and the γ contained Cr, Mo, and W such that $\text{Cr} + 1.75 (\text{Mo} + \text{W})$ is greater than 33 at.%, then minor phases such as σ -, μ -, Mo-, or W-rich BCC solutions were likely to form at 850° C (ref. 25).

The relation between increased refractory metal contents and phase instabilities in superalloys had previously been recognized in the PHACOMP (refs. 26 and 27) calculations developed to control σ formation in the mid 60's. It is suggested that the recognition of the importance of this refractory metal balance relative to the overall composition, particularly to γ' formers, has in part been responsible for the leveling or slight reduction in the refractory metal content of superalloys since the late 60's.

The influence of the refractory metals is also seen in carbide stability. Alloys which are low in Cr and high in Mo and W tend to form M_6C rather than M_{23}C_6 (ref. 28). V, Ta, and Nb, on the other hand, tend to form monocarbides - MC phases.

Niobium is known also to form Ni_3Nb , an orthorhombic or metastable tetragonal phase, which can be an effective strengthener. It is the metallurgy of Ni_3Nb which forms the strengthening basis for the alloy Inconel 718, the most widely used of all the superalloys in gas turbine engines. Mr. Boesch will describe this alloy in much greater detail later in this meeting.

It has been common to describe superalloys in terms of " γ strengtheners," " γ' formers," and "carbide formers." This is a simplification to describe the superalloy, a multicomponent alloy attempting to achieve equilibrium among as many as five phases. We suggest that these simplified descriptions be applied with caution. Since most

[†]MAR-M is a tradename of Martin Metals Company.

of the phases have significant solubility for a variety of metals, simple additions of elements can cause a variety of complex results. For example, consider the relative solubilities of Mo, W, Ta, and Nb in both the γ and γ' phases. Typical partitioning ratios for several refractory metals are shown in table III. One might also use these data to differentiate γ' formers from γ formers. If the ratio is less than unity (i.e., 1:1), the element tends to stabilize γ (i.e., Cr, Mo). The converse is true of γ' stabilizers. While the refractory metals Nb, Ta, and V are strong γ' stabilizers, Mo is a weak γ stabilizer and W has no significant tendency toward either phase. The partitioning of Re has not been definitely established, although its increase in strengthening effect relative to W is reported to be associated with an increase in misfit energy (ref. 16).

Thus, when considering the alloying effect of the refractory elements, one must recall the complex nature of the Ni-base superalloys. The alloy addition will alter the carbides, change the amount of γ' and the misfit between the γ' and γ and thus affect properties. Further, if excessive amounts of the refractory elements are used, additional phases such as the BCC solid solutions, σ , or μ may form.

COSAM PROGRAM

The rationale for undertaking the COSAM Program was given in the introduction section of this paper while the history of refractory metal alloying brought out the importance of these metals in today's superalloys used in the aerospace industry. Three (Cr, Ta, and Nb) of the seven refractory metals previously discussed are being addressed within the COSAM Program. The basis for this focus is primarily the net import reliance of the United States on each of the refractory metals as shown in Fig. 7. In 1982 the United States imported 88 percent of the required Cr with the remaining 12 percent coming from recycled material. Similarly 93 percent of the Ta consumed by the United States was imported with recycled material contributing 7 percent to the required needs. All Nb used in the United States was imported. In contrast, as shown in Fig. 7, the United States is a net exporter of Mo and imports only 14 percent of the required V. Although W in 1982 showed a 48 percent import dependence, it has been estimated by U.S. mining companies that the United States can become self-sufficient in this metal within two to three years. Re had initially been considered for inclusion in the COSAM Program. However, because of its limited use to date in the aerospace industry, programs have not been initiated to replace Re in Ni-base superalloys.

NASA plans to accomplish the general objectives of the COSAM Program outlined in the Introduction by creating the understanding needed to minimize the use of strategic metals in advanced aerospace systems. This program is being undertaken via two major research thrusts: strategic element substitution and alternative material

identification. A smaller effort also is under way involving advanced processing concepts. Results from the research and any required supporting technology will help create the materials technology options needed to allow industry to make trade-offs in material properties for critical components versus the cost and availability effects of their strategic metal content. Conservation, as well as reduced dependence on strategic metals, will be achieved in the area of strategic element substitution by systematically examining the effects of replacing tantalum and niobium with less strategic elements in current, high-use engine alloys. This will help guide future material specifications if one or more of these metals becomes in short supply, and will create a powerful base of understanding that will benefit all future advanced alloy development. And in the longer term, the development (higher risk) of alternative materials that can replace most strategic metals with others readily available in the U.S. could lead to a dramatic reduction in the U.S. dependence on foreign sources. This later technology area will help conserve all four strategic metals: Cr, Ta, Nb, and Co.

The various efforts are being conducted under the overall programmatic management of the NASA Lewis Research Center. Some of this work is being conducted in-house at Lewis. In addition, cooperative programs involving Lewis working together with both industry and universities in tripartite projects are under way to optimize the utilization of the expertise at each of the various organizations and to seek synergistic results from these combined efforts. In the following section, COSAM Program research efforts will be presented and initial results discussed.

PRESENT COSAM EFFORTS ON REFRACTORY METALS IN SUPERALLOYS

STRATEGIC ELEMENT SUBSTITUTION - As part of NASA's COSAM Program, the influence of strategic refractory metals on the properties and microstructure of Ni-base superalloys is presently being examined. The goals of this research are to provide a basic understanding of the mechanisms by which the refractory metals strengthen the superalloys and to provide effective substitutes for alloying additions that may become limited in supply. Currently, programs examining the roles of Ta and Nb on several alloys are in various stages of progress.

The influence of Ta on the creep resistance of single crystal superalloys is currently being investigated by Nathal and Ebert (ref. 30). The alloy NASAIR 100 is a modification of MAR-M 247 designed for single crystal applications and contains 3 wt% Ta and 10 wt% W among other alloying additions (ref. 31). Alloys were prepared with the Ta content removed (i.e., with Ni substituted for Ta or with W substituted for Ta).

Nathal and Ebert's results showed that the removal of Ta caused large decreases in the γ' solvus temperature and the amount of γ' phase, which is consistent with the known tendency of Ta to partition strongly to the γ' phase. Substi-

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tution of W for Ta caused a small decrease in the percentage of γ' and the γ' solvus, evidently because W does not partition strongly to the γ' phase. The decrease in γ' volume fraction from 51 to 45 vol% can be seen in the scanning electron micrograph in Fig. 8. The substitution of Ni for Ta also caused large decreases in yield strength, ultimate tensile strength, and creep life, as indicated in Fig. 9. Substitution of W for Ta caused slight reductions in tensile properties but actually improved the creep life compared to the standard 3 wt% Ta alloy. These higher strength alloys had lower tensile ductilities, but the lowest ductility of 20 percent elongation appears to be adequate. The strengthening effect of Ta and W appears to be at least partially caused by the increase in the amount of γ' precipitate, which results from the high Ta and W levels. It is apparent that high refractory metal levels are essential for high temperature strength of superalloy single crystals. However, further work is necessary to determine the relative effectiveness of the different elemental additions.

The role of Ta in other alloys is also being studied. In B-1900 + Hf, reduction of Ta from the standard 4.3 wt% level actually increased creep life (ref. 32). However, extensive testing is necessary to clarify these results. Other studies are under way by Heckel et al. (ref. 33) on the role of Ta in the mechanical properties and oxidation resistance of MAR-M 247. They are examining the influence of Ta on equiaxed polycrystal, directionally solidified polycrystal, and single crystal versions of the alloy. Because Ta is known to be a strong carbide former, different carbon levels will also be investigated in the single crystal alloys. Since this investigation was started only recently, much of the work remains to be reported. However, preliminary results have shown that Ta has significant effects on the carbide and γ' lattice parameters and on the $\gamma - \gamma'$ lattice mismatch. Ta additions also appear to be beneficial for reducing the reaction zone between the substrate alloy and its protective coating, as illustrated in Fig. 10.

Finally, the influence of Nb on the superalloy Inconel 718 is also being examined. This study by Ziegler and Wallace (ref. 34) is also in its early stages and few results are presently available. The basic outline of the study is to investigate whether various combinations of the nonstrategic refractory metals W, Mo, and V could be substituted for all or part of the Nb in this alloy. Initial mechanical property results indicated that reductions in Nb content may not be feasible unless sacrifices in strength are tolerable.

ALTERNATIVE MATERIALS IDENTIFICATION - A second major thrust of the COSAM Program is research on alternative materials such as intermetallic compounds and advanced Fe-base alloys. Research is under way on Fe aluminides and Ni aluminides as potential structural materials of the future. Although the risk is high because of the lack of near-room-temperature ductility

in these materials, their high melting points offer a high payoff. Efforts are focused on understanding the high temperature deformation mechanisms of the binary aluminides; alloying to improve high temperature creep properties; and improving low temperature ductility via processing to achieve grain refinement.

Results of grain size effects on creep of FeAl by Whittenberger (ref. 35) are shown in Fig. 11 and on low temperature ductility of NiAl by Schulson (ref. 36) in Fig. 12. The ordered FeAl intermetallic exhibited the unusual behavior of improved creep resistance with decreasing grain size at temperatures up to $0.75 T_m$. Grain refinement through thermomechanical processing was shown to lower the ductile-brittle transition temperature of NiAl (fig. 12).

Research on Fe-base alloys includes SiC fiber strengthening of a nonstrategic-metal-content matrix (ref. 37) and alloy development in the Fe-Cr-Mn-C system (ref. 38). In regard to the later, results by Lemkey suggest that equiaxed or aligned grain structures of an Fe - 20 wt% Cr - 10 wt% Mn - 3.2 wt% C alloy offers potential as a high temperature structural material as shown in Fig. 13.

ADVANCED PROCESSING CONCEPTS - A small effort is under way as part of the COSAM Program in the area of advanced processing concepts. The purpose of one of these efforts is to conserve strategic materials via tailored fabrication as suggested in Fig. 14. An Fe alloy such as Inconel 901 could be used as the hub of a disk, which operates at lower temperatures, while René 95 could be used in the rim of the disk, where its higher temperature capabilities are required. As noted by the refractory metal content of these alloys, a slight savings in Cr would be achieved by this technique and Nb could be totally eliminated from the disk hub. Research efforts are focused on the interface stability of the two alloys, and initial tensile results by Harf suggest this approach offers possibilities (ref. 39).

A study of the possible reduction in the use of Cr in Ni-base superalloys is in progress by the combined approaches of both elemental substitution and rapid solidification processing (RSP) (ref. 40). Unique microstructures achieved by RSP may permit a reduction in the Cr content normally required in current nickel-base superalloys.

A final program aimed at offsetting the strategic nature of Nb by providing an alternative source is being evaluated on a laboratory scale. A large potential source of Nb for aerospace alloys could be Sn slags. An investigation was initiated by Dreshfield and Johnson (ref. 41) to determine the effects of Sn additions to Inconel 718 since it constitutes the largest single use of Nb in the aerospace field. Their results suggest that rupture life of Inconel 718 as shown in Fig. 15 is not impaired with the addition of up to 1000 ppm by weight of Sn, a level considered beyond that which would be encountered by using Sn slags as a source of Nb. Scale-up to commercial-size heats will be required to further validate the initial laboratory data.

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CONCLUDING REMARKS

We have presented in this paper the U.S. import position with regard to several critical and strategic aerospace materials. It was further shown through tracing the history of the use of refractory metals and their role in Ni-base superalloys that they play a key role in the high temperature strength and environmental resistance of Ni-base superalloys. The COSAM Program is so constituted that its primary purpose is to understand the roles of critical and strategic elements in superalloys through basic research efforts within NASA Lewis Research Center, universities, and industry. By gaining this understanding and identifying alternative materials or utilizing advanced processing concepts, technology will be available to circumvent possible future shortages of materials or price escalations that may occur. This "on the shelf" technology may further help reduce the normal 6 to 9 years required to introduce a new material into gas turbine engines (refs. 42 and 43). The refractory metals Cr, Ta, and Nb are currently a part of the COSAM Program emphasis primarily because of the near 100 percent import reliance of the United States on these metals and the key roles they play in the aerospace industry. We believe that their use will continue at their current levels of concentration in superalloys as long as the foreign sources for each of them remains stable. However, if a critical and strategic material supply crisis does occur in these three refractory metals, the COSAM Program will provide technological alternatives.

REFERENCES

1. Mineral Commodity Summaries 1983, Bureau of Mines, Washington, D.C., 1983.
2. Monthly Digest of Significant Developments in Strategic Metals Intelligence, p. 3, B. O. Szuprowicz, October 1981.
3. Kenneth R. Sheets: U.S. News and World Report, 1982, vol. 92, p. 59.
4. Aerospace, 1982, vol. 20, pp. 13-17.
5. Joseph R. Stephens: NASA TM-81617, NASA Lewis Research Center, Cleveland, OH, October 1980.
6. Joseph R. Stephens: NASA TM-82662, NASA Lewis Research Center, Cleveland, OH, June 1981.
7. Joseph R. Stephens: NASA TM-82852, NASA Lewis Research Center, Cleveland, OH, May 1982.
8. Joseph R. Stephens: COSAM Program Overview, pp. 1-11, NASA TM-83006, NASA Lewis Research Center, Cleveland, OH, October 1982.
9. W. Betteridge and J. Heslop, eds.: The Nimonic Alloys, 2nd ed., pp. 7-22, Crane, Russak & Company, New York, 1974.
10. William Campbell: A List of Alloys with Physical Properties of Typical Alloys, American Society for Testing Materials, Philadelphia, PA, 1930.
11. C. H. Lund: DMIC Report 153, Defense Metals Information Center, Battelle Memorial Institute, May 5, 1961.
12. H. E. Collins, R. J. Quigg, and R. L. Dreshfield: ASM Trans. Q., 1968, vol. 61, pp. 711-721.
13. John C. Freche and William J. Waters: NASA TN D-1531, NASA Lewis Research Center, Cleveland, OH, April 1963.
14. Angela Lee, A. Linder, and A. J. Perry: J. Mater. Sci., 1974, vol. 9, pp. 164-167.
15. H. E. Collins: TRW Technical Memorandum TM-4455, TRW Equipment Laboratories, Cleveland, OH, January 4, 1969.
16. L. S. Lin, A. F. Giamei, and R. E. Doiron: Proc. Electron Microsc. Soc. Amer., 1980, vol. 38, pp. 330-331.
17. P. Aldred: SAE Paper 751049, Society of Automotive Engineers, Warrendale, PA, November 1975.
18. M. Gell, D. N. Duhal, and A. F. Giamei: in Superalloys 1980, Proceedings of the Fourth International Symposium on Superalloys, John K. Tien, Stanley T. Wlodek, Hugh Morrow III, Maurice Gell, and Gernant E. Maurer, eds., pp. 205-214, American Society for Metals, Metals Park, OH, 1980.
19. Chester T. Sims and William C. Hagel, eds.: The Superalloys, John Wiley & Sons, New York, 1972.
20. Elihu F. Bradley, comp.: Source Book on Materials for Elevated-Temperature Applications, American Society for Metals, Metals Park, OH, 1979.
21. G. P. Sabol and R. Stickler: Phys. Status Solidi, 1969, vol. 35, pp. 11-52.
22. R. L. Dreshfield and J. F. Wallace: Metall. Trans., 1974, vol. 5, pp. 71-78.
23. Max Hansen: Constitution of Binary Alloys, 2nd ed., McGraw-Hill Book Company, New York, 1958.
24. Rodney P. Elliott: Constitution of Binary Alloys, First Supplement, McGraw-Hill Book Company, New York, 1965.
25. R. L. Dreshfield: Applications of Phase Diagrams in Metallurgy and Ceramics, vol. 1, G. C. Carter, ed., pp. 624-659, NBS SP-496, National Bureau of Standards, Washington, D.C., 1978.
26. William J. Boesch and John S. Slaney: Met. Prog., 1964, vol. 80, pp. 109-111.
27. L. R. Woodyatt, C. T. Sims, and H. J. Beattie, Jr.: Trans. Metall. Soc. AIME, 1966, vol. 236, pp. 519-527.
28. R. L. Dreshfield: ASM Trans. Q., 1968, vol. 61, pp. 352-354.
29. Owen H. Kriege and J. M. Baris: ASM Trans. Q., 1969, vol. 62, pp. 195-200.
30. Michael V. Nathal and L. J. Ebert: COSAM Program Overview, pp. 107-116, NASA TM-83006, NASA Lewis Research Center, Cleveland, OH, October 1982.
31. T. E. Strangman, G. S. Hoppin III, C. M. Phipps, K. Harris, and R. E. Schwer: in Superalloys 1980, Proceedings of the Fourth International Symposium on Superalloys, John K. Tien, Stanley T. Wlodek, Hugh

Stephens, Dreshfield, Nathal

- Morrow III, Maurice Gell, and Gernant E. Maurer, eds., pp. 215-224, American Society for Metals, Metals Park, OH, 1980.
32. C. S. Kortovich: COSAM Program Overview, pp. 125-131, NASA TM-83006, NASA Lewis Research Center, Cleveland, OH, October 1982.
 33. R. W. Heckel, B. J. Pletka, D. A. Koss, and M. R. Jackson: COSAM Program Overview, pp. 117-123, NASA TM-83006, NASA Lewis Research Center, Cleveland, OH, October 1982.
 34. Karl Ziegler and John F. Wallace: COSAM Program Overview, pp. 133-140, NASA TM-83006, NASA Lewis Research Center, Cleveland, OH, October 1982.
 35. J. Daniel Whittenberger: COSAM Program Overview, pp. 163-174, NASA TM-83006, NASA Lewis Research Center, Cleveland, OH, October 1982.
 36. E. M. Schulson: COSAM Program Overview, pp. 175-182, NASA TM-83006, NASA Lewis Research Center, Cleveland, OH, October 1982.
 37. Donald W. Petrasek: COSAM Program Overview, pp. 225-230, NASA TM-83006, NASA Lewis Research Center, Cleveland, OH, October 1982.
 38. Franklin D. Lemley: COSAM Program Overview, pp. 203-208, NASA TM-83006, NASA Lewis Research Center, Cleveland, OH, October 1982.
 39. Fredric H. Harf: COSAM Program Overview, pp. 141-152, NASA TM-83006, NASA Lewis Research Center, Cleveland, OH, October 1982.
 40. H. D. Fraser and B. C. Muddl: COSAM Program Overview, pp. 153-156, NASA TM-83006, NASA Lewis Research Center, Cleveland, OH, October 1982.
 41. Robert L. Dreshfield and Walter Johnson: COSAM Program Overview, pp. 157-160, NASA TM-83006, NASA Lewis Research Center, Cleveland, OH, October 1982.
 42. Joseph R. Stephens and John K. Tien: NASA TM-83395, NASA Lewis Research Center, Cleveland, OH, May 1983.
 43. Cobalt Conservation Through Technological Alternatives, publ. NMAB-406, National Academy Press, Washington, D.C. (1983.)

Stephens, Dreshfield, Nathal

TABLE I. - REFRACTORY METAL CONTENT OF SELECTED
NICKEL-BASE SUPERALLOYS AND YEAR OF AVAILABILITY

Alloy	Nominal refractory metal content, wt%							Year*
	Cr	Mo	W	Nb	Ta	Re	V	
Nimonic 80A	20	0	0	0	0	0	0	1942
Waspaloy	19	4.4	↓	↓	↓	↓	↓	1951
Nimonic 100	11	5	↓	↓	↓	↓	↓	1953
M-252	20	4.0	↓	↓	↓	↓	↓	1953
Inconel 713C	12	4.5	↓	2.0	↓	↓	↓	1956
Inconel 718	19	3	↓	5.0	↓	↓	↓	1960
TRW-NASA VIA	6.1	2	5.8	.5	9	↓	.5	1968
René 150	5	1	5	0	6	2.2	3	1978
P&WA 454	10	4	0	0	12	0	0	1980

*Approximate year of availability.

TABLE II. - MAXIMUM SOLUBILITY OF THE REFRACTORY
METALS IN NICKEL

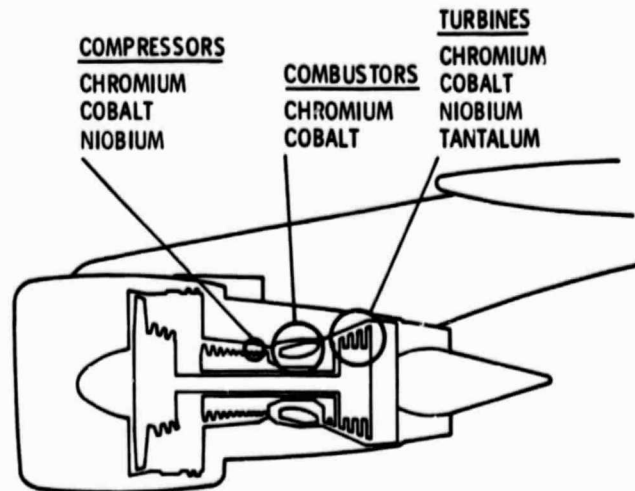
Element	Maximum solubility		Temperature at maximum solubility, °C	Ref.
	at.%	wt%		
V	43	39.6	1200	23 ↓ 24
Nb	14	20.5	1270	
Ta	15.4	35.9	1360	
Cr	50	47	1345	
Mo	27	37.5	1315	
W	17.5	40	1500	
Re	29.8	55	1600	

TABLE III. - AVERAGE GAMMA
PRIME PARTITIONING RATIOS
FOR THE REFRACTORY METALS
PLUS ALUMINUM AND TITANIUM

Element	Partitioning ratio*
V	1 : < 0.05
Nb	1 : < 0.05
Ta	1 : < 0.05
Cr	1 : 7.1
Mo	1 : 3.0
W	1 : 1.1
Al	1 : 0.24
Ti	1 : 0.10

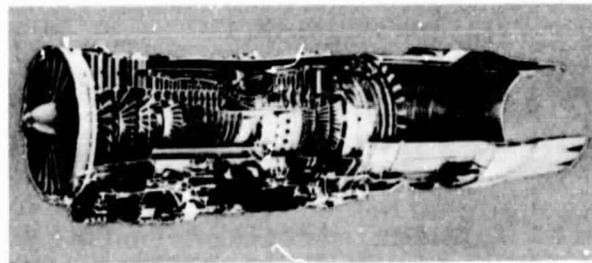
*Weight fraction in γ' /
weight fraction in γ .

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NEEDED FOR PERFORMANCE AND LONG LIFE
COBALT - HIGH TEMPERATURE STRENGTHENER
NIOBIUM - INTERMEDIATE TEMPERATURE STRENGTHENER
TANTALUM - OXIDATION RESISTANCE, STRENGTHENER
CHROMIUM - CORROSION RESISTANCE

Figure 1. - Dependence of gas turbine engines on strategic materials.



CHROMIUM, 675 kg	NIOBIUM, 65 kg
COBALT, 400 kg	TANTALUM, 2 kg

Figure 2. - F100 engine strategic material input requirements.

The graph illustrates the volatility of metal prices compared to the general consumer price index. The metals price trend shows three major peaks: a sharp rise in 1970, a peak in 1975, and a very high peak in 1980. The CPI shows a much more gradual and steady increase over the same period.

Year	Price Trend (15 Selected Metals)	CPI (Consumer Price Index)
1968	~50	~50
1970	~500	~70
1972	~100	~100
1974	~200	~130
1976	~150	~160
1978	~200	~190
1980	~950	~220
1982	~700	~250
1984	~600	~280

1a	2a	3a	4a	5a	6a	7a		8		1b	2b	3a	4a
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Figure 4 - Refractory metals used in nickel-base superalloys.

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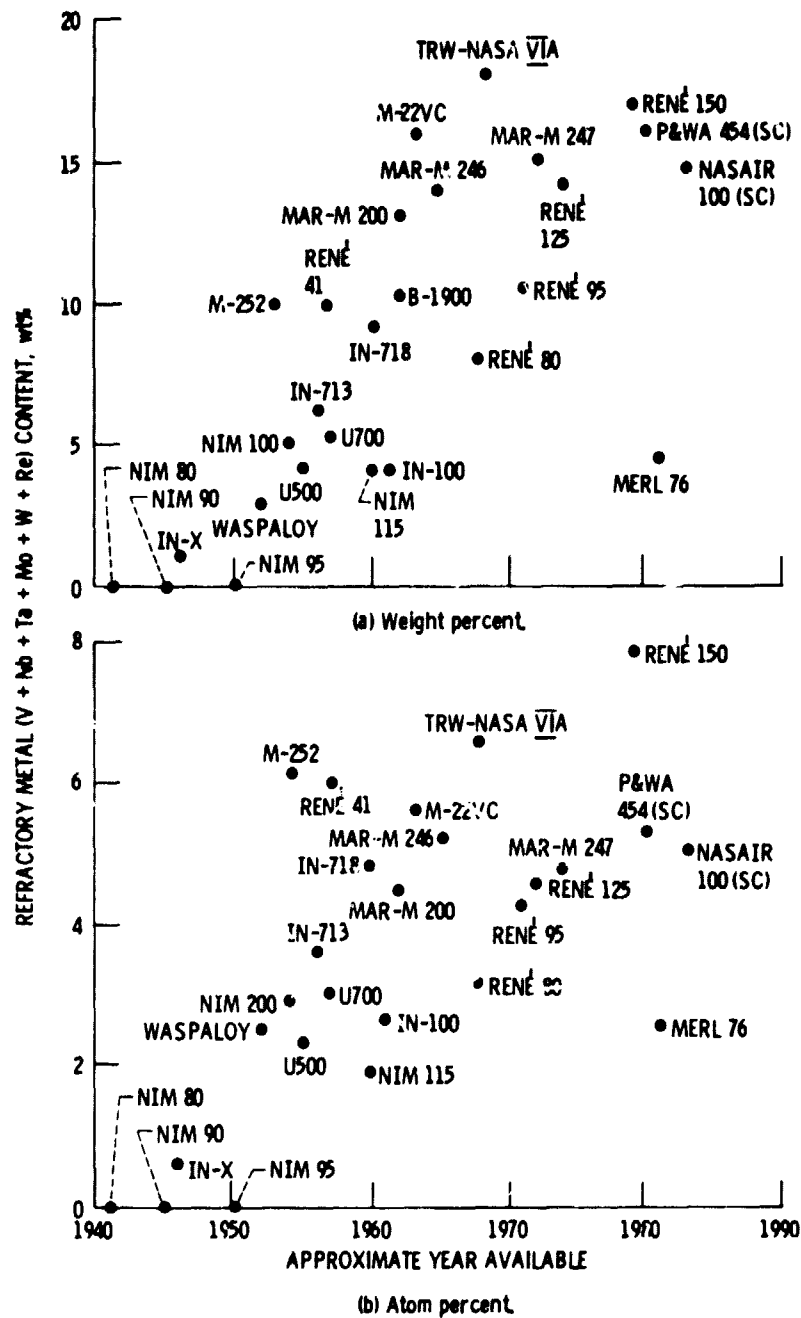


Figure 5. - Increased use of refractory metals in nickel-base superalloys.

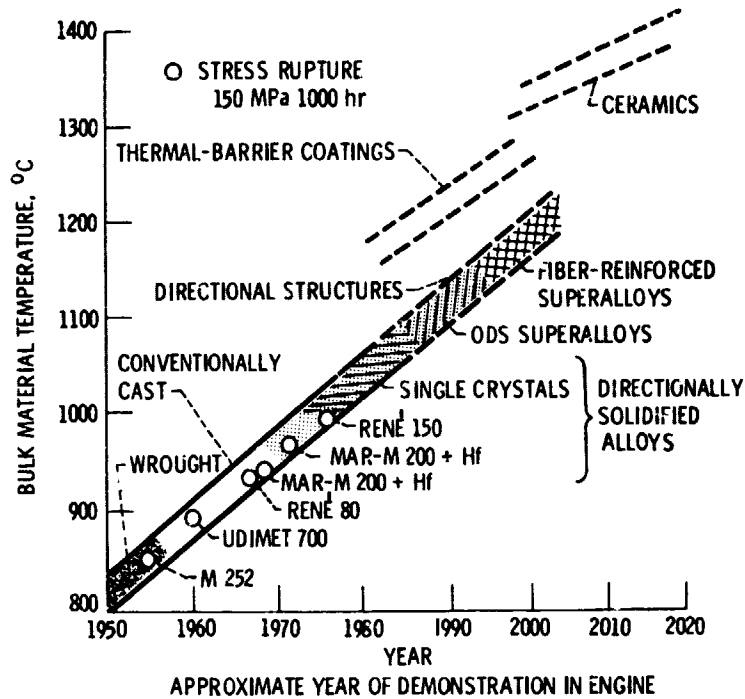


Figure 6. - Progress in turbine blade materials.

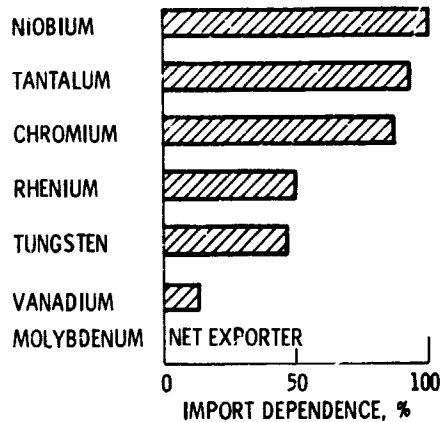


Figure 7. - U. S. import dependence of the refractory metals (ref. 1).

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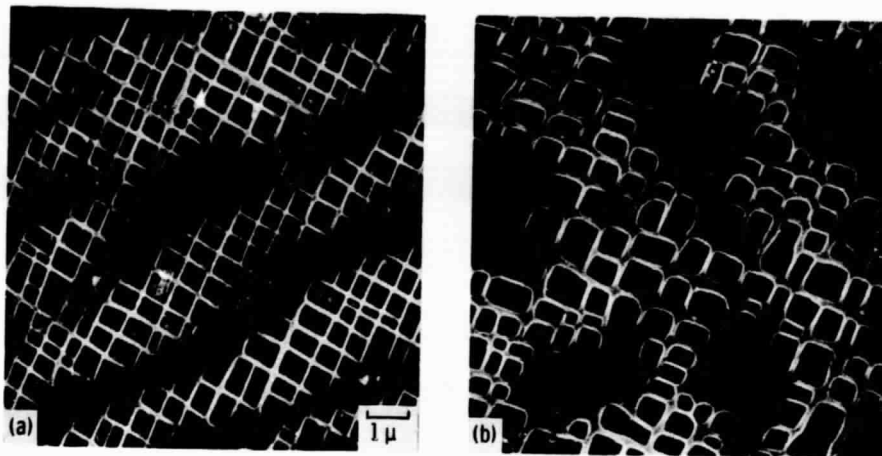


Figure 8. - Microstructure of superalloy single crystals with (a) 3 w/o Ta and (b) 0 w/o Ta. (ref. 30).

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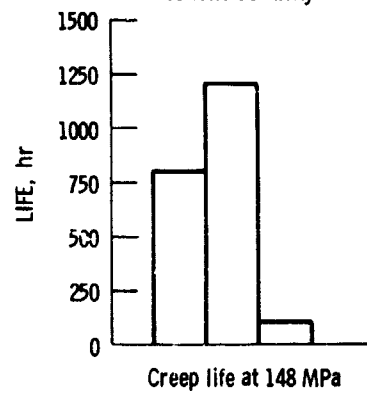
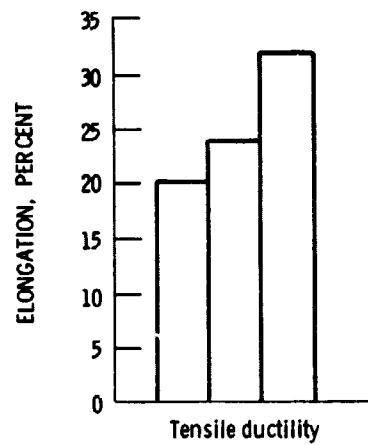
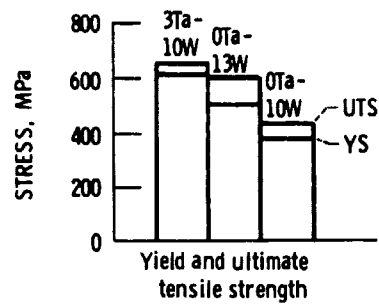
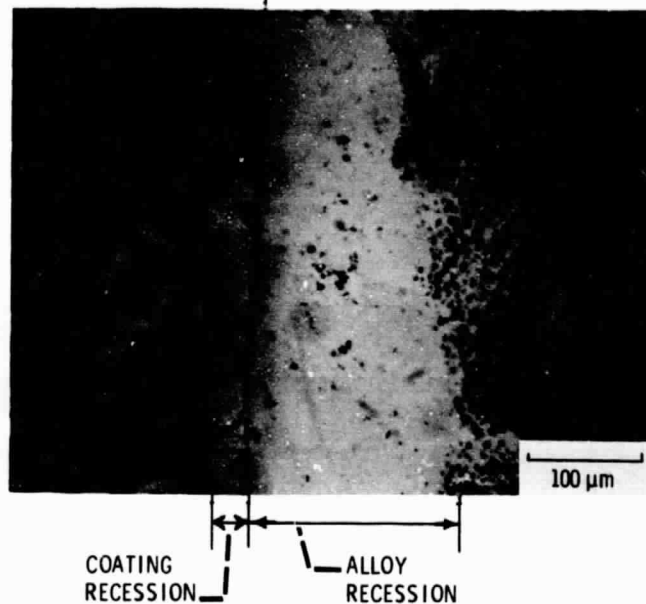
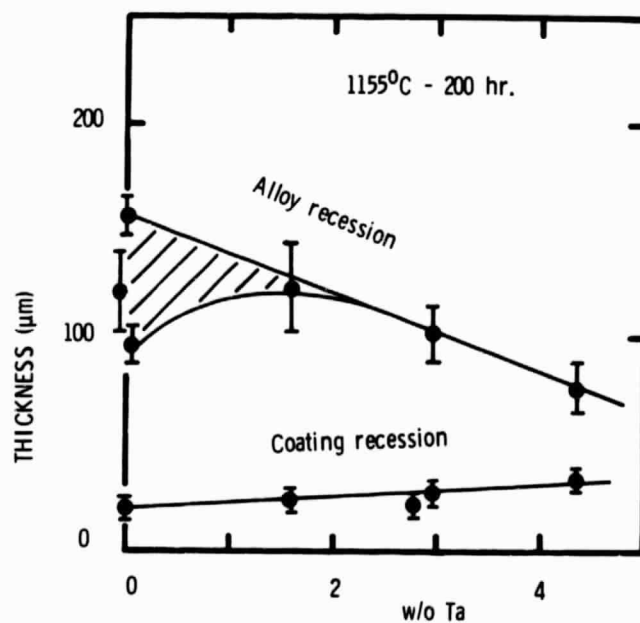


Figure 9. - Effects of substituting Ni and W for Ta in MAR-M247 single crystals tested at 1000° C. (Ref. 30.)

Ni-13w/o Al 14w/o Cr
(0.13w/o Zr) | Mar M 247



(a) Typical microstructure, 1155°C - 200 hr.



(b) Effect of Ta on the depth of reaction zone. (ref 33).

Figure 10. - Influence of Ta levels in MARM 247 on the application of a protective coating.

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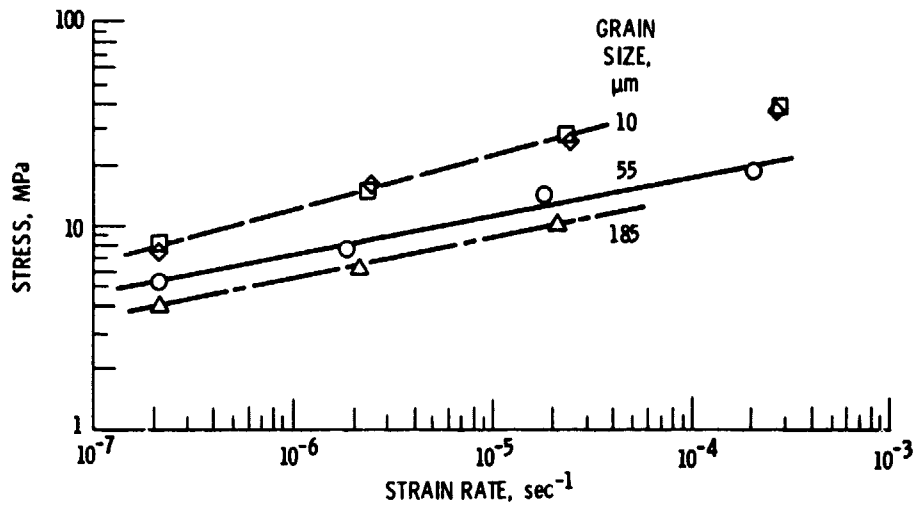


Figure 11. - Flow stress-strain rate behavior for several Fe-40Al materials at 925°C.

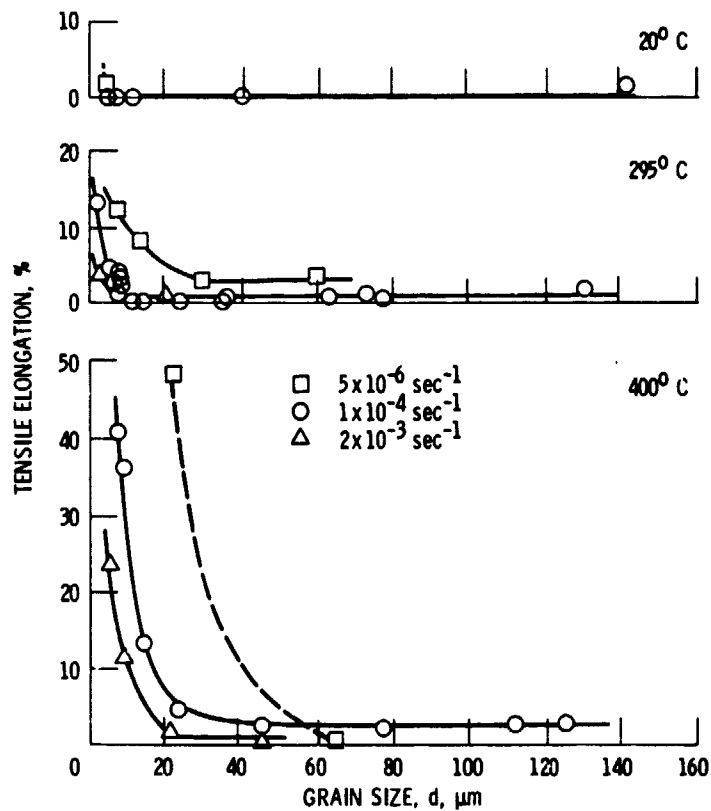


Figure 12. - Tensile elongation of binary NiAl deformed at various temperatures and strain rates.

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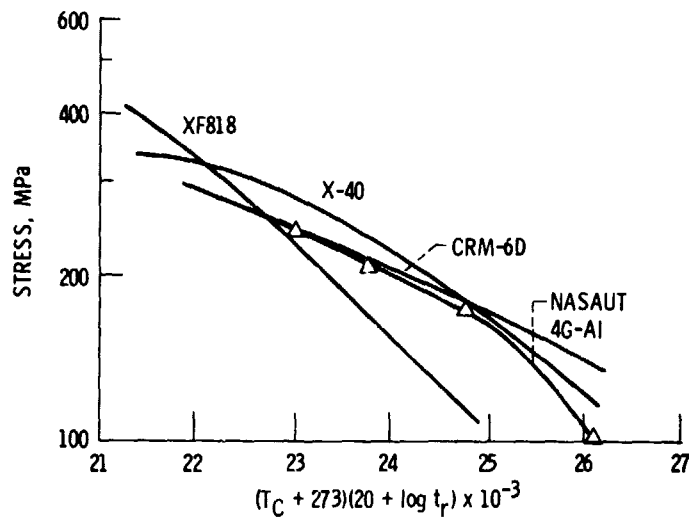


Figure 13. - Stress-rupture strength of experimental iron-base alloy NASAUT 4G-Al compared to commercial iron- and cobalt-base alloys.

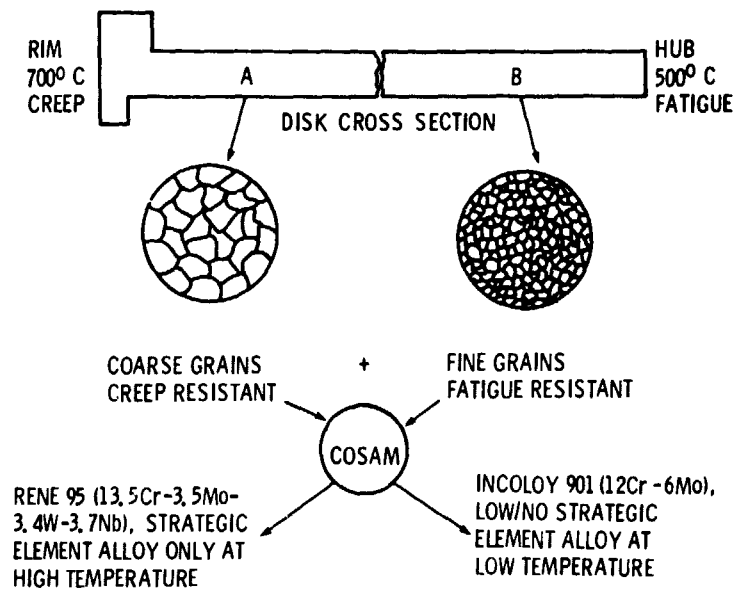


Figure 14. - Dual-alloy joining technology for turbine disks.

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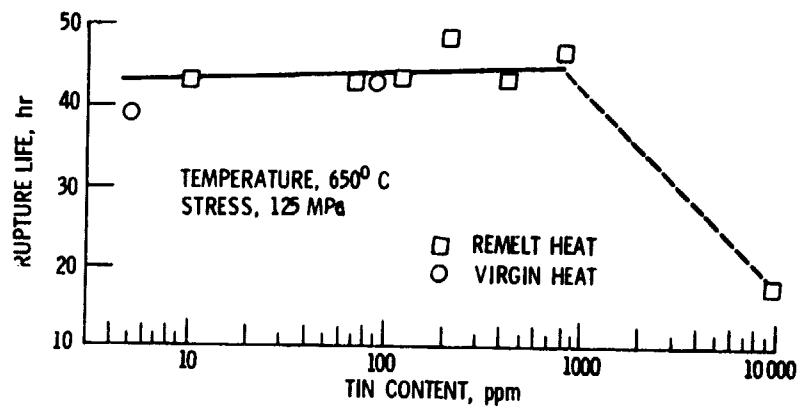


Figure 15. - Effect of tin content on rupture life of Inconel 718.